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# The emission spectroscopy of AlD in the visible region: experimental and theoretical investigations

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## Abstract

The emission spectrum of the AlD isotopologue has been experimentally studied using Fourier transform spectroscopy in the 17,700 – 28,500 cm<sup>-1</sup> spectral region. AlD molecules were produced within an aluminum hollow-cathode lamp with two anodes in the presence of 2.7 Torr of Ne and 0.2 Torr of ND<sub>3</sub>. The observed bands have been assigned to the A<sup>1</sup>Π–X<sup>1</sup>Σ<sup>+</sup> (0 – 0, 1 and 1 – 0, 1, 2, 3 bands) and C<sup>1</sup>Σ<sup>+</sup>–A<sup>1</sup>Π (0 – 0 and 1 – 1 bands) transitions. In total, more than 450 rotational frequencies were measured with an absolute accuracy of about 0.002 cm<sup>-1</sup>. The current data have been combined with available measurements of the pure rotational lines by Halfen and Ziurys [Astrophys J 2010;713:520-523] and with the ro-vibrational bands by White *et al.* [J Chem Phys 1993;99:8371-8378] to provide improved spectroscopic constants of the X<sup>1</sup>Σ<sup>+</sup>, A<sup>1</sup>Π and C<sup>1</sup>Σ<sup>+</sup> states of AlD. These results match closely theoretical values obtained using a new set of *ab initio* potentials calculated with a spin-orbit Hamiltonian.

*Key words:* AlD isotopologue, Visible spectrum, Fourier transform spectroscopy, Rotational analysis, Molecular parameters, *ab initio* quantum

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## 1. Introduction

The AlH molecule, along with its isotopologue AlD, is one of the most studied metal-bearing diatomic hydrides because of its importance in astrophysics [1, 2, 3, 4, 5, 6, 7, 8, 9, 10] and chemistry [11, 12, 13]. In addition both the neutral AlH molecule [14] and AlH<sup>+</sup> ion [15, 16, 17, 18] are very promising candidates for laser cooling [19].

The emission spectrum of AlD was first observed by Holst and Hulthén [20] in 1934. The study was focused on the rotational analysis of the eight bands (0–0, 1; 1–0, 1, 2, 3; 2–1, 2) of the prominent A<sup>1</sup>Π–X<sup>1</sup>Σ<sup>+</sup> system. The rotational term values for the observed vibrational levels, band origin values and estimated values of the main molecular constants for the A<sup>1</sup>Π,  $v = 0, 1, 2$  and X<sup>1</sup>Σ<sup>+</sup>,  $v = 0, 1, 2, 3$  levels of AlD were obtained and reported. The authors have also observed a few rotational transitions beyond the predissociation limit in the A<sup>1</sup>Π state by using the arc-discharge technique in high deuterium pressure conditions. The predissociation data were used by Herzberg and Mundie [21] to estimate the dissociation energies of AlH and AlD. The predissociation phenomena in the A<sup>1</sup>Π state were also investigated by Olsson [22] at the low pressure discharge.

In 1948, Nilsson [23] supplemented previous measurement by recording many new lines, including lines beyond the predissociation limit in the A<sup>1</sup>Π state of the eight bands first observed by Holst and Hulthén [20]. He also discussed the pressure effect in the A<sup>1</sup>Π–X<sup>1</sup>Σ<sup>+</sup> system bands of AlH and AlD, observed in the arc-discharge.

The first rotational analysis of the C<sup>1</sup>Σ<sup>+</sup>–A<sup>1</sup>Π system of AlD includes the work of Balfour and Lindgren [24] in which they investigated the 0 – 0 and 1 – 1 bands. The bands were recorded up to the predissociation limit in the A<sup>1</sup>Π state, with the reciprocal dispersion of 0.5 Å/mm. The resulting set of molecular constants for the C<sup>1</sup>Σ<sup>+</sup>,  $v = 0, 1$  levels confirms the very early results given by Grabe and Hulthén [25] and by Khan [26] from investigation of the C<sup>1</sup>Σ<sup>+</sup>–X<sup>1</sup>Σ<sup>+</sup> system.

In the infrared, the ro-vibrational bands of the ground state of AlD were observed in absorption by Urban and Jones [27] using diode laser spectroscopy and in emission by White *et al.* [28] using Fourier transform (FT)

spectroscopy. The experiments covered the same seven vibrational sequences, from  $1-0$  to  $7-6$ , in the  $X^1\Sigma^+$  state. The emission spectrum [28] was much richer, specifically with many high- $J$  value lines measured. Both studies resulted in the Dunham constants ( $Y_{ij}$ ) for the  $X^1\Sigma^+$  state of AlD as well as the mass-independent Dunham coefficient ( $U_{ij}$ ) and mass scaling coefficients ( $\Delta_{ij}$ ) for the ground state of AlH. The former works show that the spectroscopy of the AlH and AlD isotopologues can efficiently support the investigation of the effects of breakdown in the Born-Oppenheimer approximation in diatomic molecules containing hydrogen.

Halfen and Ziurys [29, 30] measured the pure rotational transitions of the AlD  $X^1\Sigma^+$  state ( $J = 2 \leftarrow 1$  and  $J = 3 \leftarrow 2$ ) by submillimeter direct absorption method near the 393.6 and 590.3 GHz regions. The rotational, electric quadrupole and nuclear spin-rotation constants were determined for the AlD isotopologue.

Although widely studied experimentally, there have been relatively few theoretical studies of AlD. Calculations of the vibration-rotational line strengths for the  $X^1\Sigma^+$  state have been carried out by Tipping *et al.* [31] in 1978. The hyperfine constants, rotational and vibration-rotation coupling constants as well as anharmonic vibrational frequencies for the ground state of AlH and AlD were recently calculated by Brown and Wasylishen [32]. The authors also widely compared present results with available previous theoretical and experimental data for the ground state of both isotopologues.

The present paper is a result of continuation of our recent spectroscopic studies on the emission spectra of AlH [33, 34, 35, 36], AlH+ [37] and AlD [38] by high accuracy dispersive optical spectroscopy. The visible (VIS) spectra of the  $A^1\Pi-X^1\Sigma^+$  and  $C^1\Sigma^+-A^1\Pi$  systems of AlD are recorded by Fourier transform spectroscopy. The high-quality FT spectroscopic data provide significant improvement in wavenumber measurements for the observed bands of both systems under consideration. By including the most recent spectroscopic information on the ground  $X^1\Sigma^+$  state obtained from submillimeter [30] and infrared [28] studies, an improved set of the spectroscopic constants of the  $X^1\Sigma^+$ ,  $A^1\Pi$  and  $C^1\Sigma^+$  states of AlD was obtained. In addition, high quality *ab initio* techniques are used to produce potential energy curves of all the states recorded in the experimental study.

## 2. Experimental details and observations

The AID molecule was produced and excited by an electric discharge in a water-cooled hollow-cathode aluminium lamp with two anodes [39]. The anodes were operated at  $2 \times 400$  V,  $2 \times 60$  mA dc and an additional electric field was added between anodes in order to convert one of them into a cathode (400 V, 120 mA dc). A static mixture of the Ne buffer gas ( $\sim 2.5$  Torr) and a trace amount of ND<sub>3</sub> ( $\sim 0.2$  Torr, 99% of D<sub>3</sub>) was let into the lamp.

In the preliminary experiment we observed that AIH bands occur in the spectrum, without any additional hydrogen source in the lamp. Evidently there were enough H-containing impurities to provide a significant AIH spectrum. The still electric discharge (of about 10 hours) causes a gradual decrease of the intensity of the AIH spectrum. When the AIH bands were approximately half their initial intensity we decided to let deuterated ammonia into the lamp. Consequently, a very satisfying intensity ratio of the AID:AIH spectra was obtained (ca. 3 : 1).

A Fourier transform spectrometer (Bruker IFS 125HR), operated under vacuum conditions, was used to record the VIS spectrum of AID. The photomultiplier tube was used as an internal detector to cover the 11,000 – 32,000 cm<sup>-1</sup> spectral region. The low frequency region of observation was rejected (up to 17,700 cm<sup>-1</sup>) by using a 575 nm shortpass filter (Edmund optics) in order to block out the strong Ne lines: none of the desired bands are found in the excluded region. The use of a filter led to an approximately sixfold improvement of the signal-to-noise ratio. Therefore, the weakest A<sup>1</sup>Π–X<sup>1</sup>Σ<sup>+</sup>, 0 – 1 and C<sup>1</sup>Σ<sup>+</sup>–A<sup>1</sup>Π, 1 – 1 bands could be registered. In total, 128 scans were co-added in  $\sim 2.5$  h of integration at a resolution of 0.03 cm<sup>-1</sup>.

The spectral line positions were extracted from the observed spectrum using a data reduction program included in the Opus<sup>TM</sup> software package [40]. The peak positions were determined by fitting a Voight lineshape function to each spectral contour. The spectrum was calibrated with the measurements of the Ne atomic lines [41]. The AID lines have width of  $\sim 0.08$  cm<sup>-1</sup> and appear with a maximum signal-to-noise ratio of  $\sim 1400 : 1$  for the strongest A<sup>1</sup>Π–X<sup>1</sup>Σ<sup>+</sup>, 0 – 0 band. It limits the absolute accuracy of our measurements of the strong and unblended molecular transitions to  $\pm 0.002$  cm<sup>-1</sup>. However, the blended and/or weaker lines and the lines belonging to the weakest bands were measured with lower accuracy, which amounted to  $\pm 0.01$  cm<sup>-1</sup>.

The observed line positions of A<sup>1</sup>Π–X<sup>1</sup>Σ<sup>+</sup> and C<sup>1</sup>Σ<sup>+</sup>–A<sup>1</sup>Π systems are collected in Table 1 and 2.

Table 1: Transition frequencies (in  $\text{cm}^{-1}$ ) of the  $\text{A}^1\Pi\text{--X}^1\Sigma^+$  system bands of  $\text{AlD}$ .<sup>a</sup>

$J$	0 – 0 band			0 – 1 band <sup>w</sup>		
	$R_{11ee}(J)$	$Q_{11fe}(J)$	$P_{11ee}(J)$	$R_{11ee}(J)$	$Q_{11fe}(J)$	$P_{11ee}(J)$
0	23,543.171			22,361.25		
1	23,549.256	23,536.601		22,367.45	22,354.79	
2	23,555.091	23,536.111	23,523.474	22,373.57	22,354.59	22,341.95 <sup>b</sup>
3	23,560.670	23,535.373	23,516.434	22,379.56	22,354.26	22,335.31
4	23,565.986	23,534.381	23,509.157	22,385.43	22,353.83	22,328.59
5	23,571.026	23,533.131	23,501.641	22,391.15	22,353.26	22,321.76
6	23,575.782	23,531.614	23,493.880	22,396.74	22,352.57	22,314.84
7	23,580.238	23,529.821	23,485.874	22,402.15	22,351.73	22,307.79
8	23,584.381	23,527.742	23,477.612	22,407.40	22,350.76	22,300.64 <sup>b</sup>
9	23,588.192	23,525.363	23,469.09 <sup>b</sup>	22,412.44	22,349.62	22,293.33
10	23,591.654	23,522.670	23,460.286	22,417.28	22,348.30	22,285.91
11	23,594.746	23,519.647	23,451.200	22,421.88	22,346.78	22,278.33
12	23,597.444	23,516.276	23,441.813	22,426.22	22,345.06	22,270.60
13	23,599.724	23,512.536	23,432.111	22,430.28 <sup>b</sup>	22,343.10 <sup>b</sup>	22,262.68
14	23,601.557	23,508.404	23,422.072	22,434.02 <sup>b</sup>	22,340.87	22,254.55 <sup>b</sup>
15	23,602.91 <sup>b</sup>	23,503.854	23,411.676	22,437.43	22,338.38	22,246.21
16	23,603.77 <sup>b</sup>	23,498.860	23,400.905	22,440.47	22,335.58	22,237.62
17	23,604.062	23,493.389	23,389.727	22,443.09	22,332.42	22,228.74 <sup>b</sup>
18	23,603.77 <sup>b</sup>	23,487.409	23,378.116	22,445.26 <sup>b</sup>	22,328.89	22,219.59
19	23,602.86 <sup>b</sup>	23,480.879	23,366.037	22,446.93	22,324.94	22,210.10
20	23,601.262	23,473.761	23,353.457	22,448.05	22,320.54	22,200.25
21	23,598.933	23,466.005	23,340.335	22,448.56	22,315.64 <sup>b</sup>	22,189.96 <sup>b</sup>
22	23,595.810	23,457.563	23,326.626	22,448.43 <sup>b</sup>	22,310.17	22,179.23 <sup>b</sup>
23	23,591.830	23,448.375	23,312.283	22,447.55	22,304.08	22,167.99
24	23,586.917	23,438.380	23,297.247	22,445.88	22,297.34	22,156.20
25	23,580.989	23,427.504	23,281.456	22,443.29	22,289.83	
26	23,573.947	23,415.666	23,264.844		22,281.49	
27	23,565.68 <sup>w</sup>	23,402.773	23,247.330		22,272.22	
28		23,388.72 <sup>w</sup>	23,228.818		22,261.91 <sup>b</sup>	
29		23,373.37 <sup>w</sup>	23,209.20 <sup>w</sup>			
$J$	1 – 0 band			1 – 1 band		
	$R_{11ee}(J)$	$Q_{11fe}(J)$	$P_{11ee}(J)$	$R_{11ee}(J)$	$Q_{11fe}(J)$	$P_{11ee}(J)$
0	24,385.983			23,204.041		
1	24,391.137	24,379.413		23,209.332	23,197.607	
2	24,395.574	24,377.993	24,366.285	23,214.044	23,196.464	23,184.756
3	24,399.282	24,375.857	24,358.314	23,218.166	23,194.743	23,177.199
4	24,402.249	24,372.999	24,349.641	23,221.684	23,192.433	23,169.074
5	24,404.457	24,369.401	24,340.251	23,224.580	23,189.525	23,160.376
6	24,405.885	24,365.054	24,330.144	23,226.835	23,186.004	23,151.094
7	24,406.511	24,359.939	24,319.306	23,228.424	23,181.851	23,141.217
8	24,406.307	24,354.033	24,307.715	23,229.320	23,177.045	23,130.728
9	24,405.242	24,347.313	24,295.360	23,229.490	23,171.559	23,119.609
10	24,403.277	24,339.746	24,282.215	23,228.899	23,165.369	23,107.835
11	24,400.375	24,331.303	24,268.247	23,227.507	23,158.434	23,095.381
12	24,396.488	24,321.945	24,253.437	23,225.264	23,150.720	23,082.214
13	24,391.562	24,311.627	24,237.740	23,222.119	23,142.183	23,068.296
14	24,385.539	24,300.298	24,221.115	23,218.012	23,132.769	23,053.588
15	24,378.348	24,287.901	24,203.517	23,212.871	23,122.422	23,038.040
16	24,369.910	24,274.367	24,184.888	23,206.620	23,111.074	23,021.594
17	24,360.134	24,259.624	24,165.162	23,199.160	23,098.648	23,004.187
18		24,243.576	24,144.266	23,190.40 <sup>bw</sup>	23,085.054	22,985.743
19			24,122.112		23,070.18 <sup>w</sup>	22,966.173
20						22,945.37 <sup>w</sup>
$J$	1 – 2 band			1 – 3 band		
	$R_{11ee}(J)$	$Q_{11fe}(J)$	$P_{11ee}(J)$	$R_{11ee}(J)$	$Q_{11fe}(J)$	$P_{11ee}(J)$
0	22051.407			20927.55 <sup>w</sup>		
1	22056.837	22045.110		20933.12 <sup>bw</sup>	20921.40 <sup>w</sup>	
2	22061.819	22044.24 <sup>b</sup>	22032.52 <sup>bw</sup>	20938.371	20920.792	20909.09 <sup>w</sup>
3	22066.351	22042.925	22025.38 <sup>b</sup>	20943.301	20919.880	20902.335
4	22070.411	22041.158	22017.801	20947.898	20918.648	20895.30 <sup>b</sup>
5	22073.985	22038.930	22009.778	20952.142	20917.088	20887.935
6	22077.055	22036.222	22001.312	20956.014	20915.183	20880.274
7	22079.593	22033.020	21992.383	20959.487	20912.916	20872.279
8	22081.573	22029.298	21982.981	20962.539	20910.262	20863.945
9	22082.961	22025.032	21973.080	20965.131	20907.200	20855.245
10	22083.725	22020.194	21962.661	20967.229	20903.69 <sup>b</sup>	20846.164
11	22083.821	22014.748	21951.693	20968.789	20899.715	20836.662
12	22083.201	22008.654	21940.149	20969.76 <sup>b</sup>	20895.226	20826.72 <sup>b</sup>
13	22081.810	22001.872	21927.99 <sup>b</sup>	20970.11 <sup>b</sup>	20890.174	20816.282
14	22079.593	21994.348	21915.167	20969.76 <sup>b</sup>	20884.508	20805.327
15	22076.471	21986.021	21901.640	20968.622	20878.173	20793.793
16	22072.37 <sup>b</sup>	21976.826	21887.349	20966.65 <sup>b</sup>	20871.101	20781.627
17	22067.201	21966.69 <sup>b</sup>	21872.229	20963.73 <sup>b</sup>	20863.217	20768.753
18			21856.199		20854.42 <sup>w</sup>	20755.112
19		21943.19 <sup>bw</sup>				

<sup>a</sup> Frequencies are given to three decimal places when known to better than  $0.01 \text{ cm}^{-1}$  and to two places when less accurate.<sup>b</sup> Blended line.<sup>w</sup> Weak line or weak band.

Table 2: Transition frequencies (in  $\text{cm}^{-1}$ ) of the  $\text{C}^1\Sigma^+ - \text{A}^1\Pi$  system bands of AlD.<sup>a</sup>

$J$	0 – 0 band			1 – 1 band <sup>w</sup>		
	$R_{11ee}(J)$	$Q_{11ef}(J)$	$P_{11ee}(J)$	$R_{11ee}(J)$	$Q_{11ef}(J)$	$P_{11ee}(J)$
1	21111.14 <sup>w</sup>	21097.777	21091.085			
2	21118.561	21098.515	21085.123			
3	21126.325	21099.618	21079.531			
4	21134.439	21101.101	21074.324	21295.05	21263.45 <sup>b</sup>	
5	21142.94 <sup>b</sup>	21102.948	21069.493	21303.74	21265.90	
6	21151.733	21105.181	21065.053		21268.81 <sup>b</sup>	21230.86 <sup>b</sup>
7	21160.906	21107.786	21061.011	21322.54	21272.25 <sup>b</sup>	21227.98 <sup>b</sup>
8	21170.433	21110.775	21057.367	21332.69 <sup>b</sup>	21276.22	21225.70)
9	21180.314	21114.154	21054.133	21343.26 <sup>b</sup>	21280.70 <sup>b</sup>	21223.94 <sup>b</sup>
10	21190.547	21117.926	21051.323	21354.39	21285.75	21222.79
11	21201.143	21122.099	21048.945		21291.34	21222.19 <sup>b</sup>
12	21212.100	21126.681	21046.99 <sup>b</sup>	21378.13 <sup>b</sup>	21297.49	21222.26
13	21223.423	21131.669	21045.510		21304.24 <sup>b</sup>	21222.99 <sup>b</sup>
14	21235.119	21137.090	21044.482		21311.64	21224.32
15	21247.190	21142.936	21043.91 <sup>b</sup>			21226.42 <sup>b</sup>
16	21259.661	21149.236	21043.91 <sup>b</sup>			
17	21272.524	21156.001	21044.343			
18	21285.80 <sup>bw</sup>	21163.226	21045.321			
19		21170.96 <sup>b</sup>	21046.85 <sup>b</sup>			
20		21179.190				
21		21187.952				

<sup>a</sup> Frequencies are given to three decimal places when known to better than  $0.01 \text{ cm}^{-1}$  and to two places when less accurate.

<sup>b</sup> Blended line.

<sup>w</sup> Weak line or weak band.

### 2.1. The $A^1\Pi-X^1\Sigma^+$ transition

The six bands,  $0-0, 1$  and  $1-0, 1, 2, 3$  progressions, of the  $A^1\Pi-X^1\Sigma^+$  system of AID were observed. A search for the  $2-v''$  progression bands [20, 23] was unsuccessful, probably due to the too low discharge temperature in the lamp we used. The low-pressure discharge did not populate higher excited vibrational levels of the  $A^1\Pi$  states. The  $0-0$  band is the strongest in intensity, while the  $1-1$  band has about 40% of the intensity of the  $0-0$  band. The other off-diagonal bands are much weaker in intensity (for details see Table 3).

The rotational structure of each band of the  $A-X$  transition consists of only three branches which are degraded to the red: a single  $R-$ , a single  $Q-$ , and a single  $P-$ branch. The lines of the  $Q-$ branch have approximately twice the intensity of the corresponding lines of the  $P-$ branch and  $R-$ branch. The lines of the  $R-$ branch form a characteristic band-head. An example of the high quality spectrum of the  $A^1\Pi-X^1\Sigma^+, 1-0$  band of AID is illustrated in Fig. 1.

The  $A^1\Pi$  state is predissociated by rotation [20, 22, 21, 23]. The low-pressure discharge experiments [22, 38] report the last observed rotational levels as  $A^1\Pi, v=0, J=29$  and  $A^1\Pi, v=1, J=19$ . The same phenomenon was observed in our strongest  $0-0$  and  $1-1$  bands of the  $A^1\Pi-X^1\Sigma^+$  system. In the  $0-0$  band the last observed line is  $Q(29)$  and the  $Q(30)$  line is absent. For the  $1-1$  band the  $R(18)$ ,  $P(20)$  and  $Q(19)$  lines were recognized as the last ones. The other bands of the  $A^1\Pi-X^1\Sigma^+$  system are definitely weaker and probably have much shorter lifetimes.

Figure 1: High-resolution emission spectrum of the AID  $A^1\Pi-X^1\Sigma^+, 1-0$  band recorded with the VIS-FT spectrometer with an instrumental resolution of  $0.03\text{ cm}^{-1}$ . Signal-to-noise ratio was ca. 80 : 1.



## 2.2. The $C^1\Sigma^+-A^1\Pi$ transition

The  $C^1\Sigma^+-A^1\Pi$  system bands are very similar in structure to the  $A-X$  system bands, but they are violet degraded and formed the band-head in the  $P$ -branch (see Fig. 2). The  $C-A$  system bands were recognized as much weaker (see Table 3) and the last observed lines correspond to the  $A^1\Pi, v = 0, J = 21$  and  $A^1\Pi, v = 1, J = 15$  levels. This is considerably lower than in the work of Balfour and Lindgren [24]. The authors recorded the  $0-0$  and  $1-1$  bands of the  $C-A$  system up to predissociation limits of the  $A^1\Pi$  state.

Figure 2: High-resolution emission spectrum of the AID  $C^1\Sigma^+-A^1\Pi, 0-0$  band recorded with the VIS-FT spectrometer with an instrumental resolution of  $0.03\text{ cm}^{-1}$ . Signal-to-noise ratio was ca. 20 : 1. A few lines of the AlH  $C^1\Sigma^+-A^1\Pi, 0-0$  band, occurring in the same spectral region, are marked at the bottom.

### 3. Computational method

*Ab initio* calculations of the potential energy curves were performed at a post Hartree-Fock level using a parallel version of the MOLPRO [42] (version 2010.1) suite of quantum chemistry codes. An aug-cc-pV5Z basis set [43] was used on both atoms to describe the atomic orbitals. The active space consisted of all the valence orbitals ( $3s3p$  on Al and  $1s$  on H) and the  $4s$  Rydberg orbital on the aluminium atom (four electrons in eleven orbitals). The electron correlation was determined using both the State-Averaged Complete Active Space Self-Consistent Field [44] (SA-CASSCF) and the Multi-reference Configuration Interaction [45] (MRCI) methods (for static and dynamic correlation, respectively). Finally, the spin-orbit coupling (SO-coupling) present was determined [46] using the Breit-Pauli Hamiltonian and the same basis set, the long range value ( $r = 100a_0$ ) of  $116 \text{ cm}^{-1}$  matching closely with the experimental value for the spin-orbit separation in the ground state Al atom ( $112 \text{ cm}^{-1}$ ). The equilibrium bond length in the resulting  $X^2\Sigma^+$  state potential ( $r_e = 1.637 \text{ \AA}$ ) was a superior match to experiment [28] than the aug-cc-pV6Z calculation without SO-coupling produced previously [14] by this group.

### 4. Experimental data analysis, results and discussion

The analysis of the experimental data was performed via a least-squares fitting procedure using the PGOPHER software [47]. All the most recent experimental data for AID were incorporated into the global fit:

- the hyperfine-free  $J = 2 \leftarrow 1$ ,  $J = 3 \leftarrow 2$  and  $J = 4 \leftarrow 3$  pure rotational line positions of Halfen and Ziurys [30]<sup>1</sup>,
- the infrared measurements of the  $1 - 0$ ,  $2 - 1$ ,  $3 - 2$ ,  $4 - 3$ ,  $5 - 4$ ,  $6 - 5$  and  $7 - 6$  ro-vibrational bands of White et al. [28],
- the current FT spectroscopy measurements of the  $A^1\Pi - X^1\Sigma^+$ ,  $0 - 0$ ,  $1; 1 - 0$ ,  $1, 2, 3$  and  $C^1\Sigma^+ - A^1\Pi$ ,  $0 - 0$ ,  $1 - 1$  bands in the VIS region.

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<sup>1</sup>The frequencies calculated by D. T. Halfen are  $R_{11ee}(1) = 393,661.660(36) \text{ MHz}$ ,  $R_{11ee}(2) = 590,314.932(66) \text{ MHz}$  and  $R_{11ee}(3) = 786,755.135(122) \text{ MHz}$ .

Each data set was weighted according to their claimed global accuracy. Relative weights of 1.0, 0.01 and 0.001 are assigned to the data from Halfen and Ziurys [30], the data from White *et al.* [28] and the present FT data respectively. Within the two former data sets the uncertain frequencies of the weak and/or blended lines were individually weighted according to the obs.-calc. values published in work [28] and according to the weakened and/or overlapping lines observed in the current measurements. The last assumption led to the extremely weak  $A^1\Pi-X^1\Sigma^+, 0-1$  and  $C^1\Sigma^+-A^1\Pi, 1-1$  bands being incorporated in the fit with significantly lower global weights of 0.003 and 0.005, respectively.

The root mean square error (rmse) value of the unweighted wavenumbers used in the fit is  $0.004\text{ cm}^{-1}$  and is dominated by the uncertainties of the weakest bands mentioned above. The rmse value of the weighted residuals of the wavenumbers used in the global fit is  $0.001\text{ cm}^{-1}$ , so the fitting model acceptably reproduced the experimental data set.

In total, 930 transition frequencies, of which 465 transitions came from the present measurements, were reduced to 62 parameters (11 vibrational term values + 51 molecular constants) describing altogether 12 vibrational levels of the  $X^1\Sigma^+, v=0-7$ ,  $A^1\Pi, v=0,1$  and  $C^1\Sigma^+, v=0,1$  states of AlD.

The molecular parameters and vibrational term values of the  $X^1\Sigma^+$ ,  $A^1\Pi$  and  $C^1\Sigma^+$  states obtained from the final fit are presented and compared in Table 4, 5 and 6. The band origin values and the statistical information about analyzed bands are summarized in Table 3.

Table 3: Summary of observations of the  $A^1\Pi-X^1\Sigma^+$  and  $C^1\Sigma^+-A^1\Pi$  systems of ALD.

System	$v'-v''$	Band origin <sup>a</sup> ( $\text{cm}^{-1}$ )	Intensity <sup>b</sup>	$N^c$	$J_{\max}^d$	
					$e$ -parity	$f$ -parity
$A^1\Pi-X^1\Sigma^+$	0-0	23,536.84524(10)	1000	85	28	29
		23,536.84318(95) <sup>e</sup>				
		23,536.79 <sup>f</sup>				
	0-1	22,354.90676(58)	8.6	77	26	28
		22,354.80 <sup>f</sup>				
	1-0	24,380.11908(13)	57.5	54	18	18
		24,379.40 <sup>f</sup>				
	1-1	23,198.17670(10)	450	57	19	19
		23,198.17504(91) <sup>e</sup>				
		23,197.41 <sup>f</sup>				
$C^1\Sigma^+-A^1\Pi$	0-0	22,045.54485(18)	30.3	53	18	19
		22,044.80 <sup>f</sup>				
		20,921.69396(28)	14.2	53	18	18
	1-3	20,920.91 <sup>f</sup>				
		21,097.40843(32)	14.4	58	19	21
		21,094.36(2) <sup>g</sup>				
	1-1	21,258.6218(18)	3.7	28	15	14
		21,255.68(2) <sup>g</sup>				

<sup>a</sup> Numbers in parentheses are one standard deviation in the last digit.

<sup>b</sup> Observed intensity scaled to 1000 (in arb. units).

Estimated on the basis of the strongest  $Q$ -line of the each band.

<sup>c</sup> Total number of observed lines.

<sup>d</sup> For the  $A^1\Pi$ ,  $v = 0, 1$  levels.

<sup>e</sup> Szajna et al. [38].

<sup>f</sup> Holst and Hulthén [20].

<sup>g</sup> Balfour and Lindgren [24].

The differences between current and previous [24] band origin values for the  $0-0$  and  $1-1$  band of the  $C^1\Sigma^+-A^1\Pi$  system warrants brief comment. The main reason for discrepancies is the use in work [24] of a different Hamiltonian model for the  $C^1\Sigma^+$  and  $A^1\Pi$  states. In this approach, the rotational energy is expressed including the  $-B\Lambda^2$  term [48], where  $B$  is the rotational constant and  $\Lambda$  is the quantum number of the orbital angular momentum. The  $\Lambda$  equals 0 for the  $\Sigma$  state and 1 for the  $\Pi$  state. Therefore, the band origin values for the C–A system reported by Balfour and Lindgren [24] are smaller from the present results by the  $B_0$  value of the  $A^1\Pi$  state (about  $3\text{ cm}^{-1}$ ).

#### 4.1. Molecular constants of the $X^1\Sigma^+$ state of AlD

The individual molecular constants of the ground state of AlD were presented by Halfen and Ziurys [29, 30] and Khan [26] for the  $v = 0$  level and by Szajna *et al.* [38] for the  $v = 0, 1$  levels. Moreover, the ground state constants can be calculated from the equilibrium parameters reported by White *et al.* [28]. The current experimental results for the  $v = 0, 1, 2, 3$  levels are collected in Table 6.

Table 4: Molecular constants (in  $\text{cm}^{-1}$ ) of the  $X^1\Sigma^+$  state of AlD.<sup>a</sup>

$v$	$T_v^b$	$B_v$	$D_v \times 10^4$	$H_v \times 10^8$	$L_v \times 10^{12}$	Refs.
0	0.0 <sup>c</sup>	3.28357554(17)	0.987947(13)	0.21151(19)	-0.05481(75)	<sup>d</sup>
		3.2835794(11)	0.988040(26)	0.21242(26)	-0.05774(83)	<sup>e</sup>
		3.2835752(11)	0.98649(67)			<sup>f</sup>
		3.283	0.97			<sup>g</sup>
1	1181.942885(33)	3.21467328(31)	0.975448(15)	0.20980(19)	-0.05425(68)	<sup>d</sup>
		3.2146770(10)	0.975537(25)	0.21063(23)	-0.05683(72)	<sup>e</sup>
2	2334.574955(46)	3.14674178(41)	0.963004(15)	0.20803(17)	-0.05415(60)	<sup>d</sup>
3	3458.426235(57)	3.07976700(49)	0.950649(15)	0.20611(16)	-0.05435(52)	<sup>d</sup>

<sup>a</sup> Numbers in parentheses are one standard deviation in the last digit.

<sup>b</sup> Related to the  $X^1\Sigma^+, v = 0$  level.

<sup>c</sup> Calculated from the equilibrium parameters of White et al. [28] the  $G(0)$  value equals  $602.1324 \text{ cm}^{-1}$ .

<sup>d</sup> This work experimental results

<sup>e</sup> Szajna et al. [38].

<sup>f</sup> Halfen and Ziurys [30].

<sup>g</sup> Khan [26].

#### 4.2. Molecular constants of the $A^1\Pi$ state of $AlD$

The accurate constant values of the  $A^1\Pi, v = 0, 1$  levels, were most recently reported by Szajna *et al.* [38] from rotational analysis of the  $0-0$  and  $1-1$  bands of the  $A-X$  system of  $AlD$ . The fact, that the present measurements included many bands, involving  $v = 0, 1$  levels of the  $A$ -state, makes the current results the most accurate and reliable to date.

The present values of the main constants,  $B_{0,1}$  and  $D_{0,1}$ , are generally slightly smaller than the previous early results [20, 23] (except of the  $B_0$  constant reported by Holst and Hulthén [20]). For the  $A^1\Pi, v = 0$  level the higher order centrifugal distortion constant  $M_0$  was required. The fit of the  $A^1\Pi-X^1\Sigma^+, 0-0$  band without this constant gave an rmse value around 50% greater than that with the  $M_0$  constant incorporated.

The current value of the  $\Lambda$ -doubling constant  $q_0 = 2.2720(22) \times 10^{-3} \text{ cm}^{-1}$  can be compared with the very early value  $q_0 = 2.0 \times 10^{-3} \text{ cm}^{-1}$  [20] and recent value  $q_0 = 2.24(4) \times 10^{-3} \text{ cm}^{-1}$  [24]. In the original paper of Balfour and Lindgren [24] the negative values of the  $q_{0,1}^{A^1\Pi}$  constants were reported, probably due to the use of a different representation of the matrix elements for the constant  $q$ . For the same reason the  $H_{0,1}$  constants of the  $C^1\Sigma^+$  state had positive values [24].

The  $H_1$  and  $L_1$  constant values are approximately one order larger than those of the  $v = 0$  level. It suggests that  $A^1\Pi$  state is highly anharmonic with a shallow potential well. On the basis of *ab initio* calculations we know that only the  $v = 0, 1, 2$  levels of  $AlD$  and  $v = 0, 1$  levels of  $AlH$  [49, 14] are supported by the internuclear potential. The experimental work on  $AlD$  [20, 23] and on  $AlH$  [50, 51, 33] support the theoretical results.

Table 5: Molecular constants (in  $\text{cm}^{-1}$ ) of the  $A^1\Pi$  state of  $\text{AlD}$ .<sup>a</sup>

$v$	$T_v^b$	$B_v$	$D_v \times 10^4$	$H_v \times 10^8$	$L_v \times 10^{12}$	$M_v \times 10^{14}$	$q_v \times 10^3$	$q_{D_v} \times 10^6$	Refs.
0	23,536.84563(41)	3.162738(13)	1.6007(11)	-1.265(35)	2.67(47)	-0.599(23)	2.2721(25)	-0.4466(41)	c
		3.162839(25)	1.6136(16)	-0.693(37)	-7.33(27)		2.2816(77)	-0.467(14)	d
		3.1648(9)	1.67(3)	-0.8(3)			2.24(4)		e
		3.1653	1.688						f
1	24,380.11960(28)	3.1608	1.675				2.0		g
		2.930912(13)	2.1656(16)	-2.743(71)	-48.3(10)		2.0398(41)	-0.564(15)	c
		2.930905(48)	2.1672(64)	-2.60(30)	-51.1(44)		2.026(15)	-0.521(56)	d
		2.935(1)	2.39(4)				1.7(2)		e
		2.9354	2.467						f
		2.934	2.21						g

<sup>a</sup> Numbers in parentheses are one standard deviation in the last digit.

<sup>b</sup> Related to the  $X^1\Sigma^+$ ,  $v = 0$  level.

<sup>c</sup> This work experimental results.

<sup>d</sup> Szajna et al. [38].

<sup>e</sup> Balfour and Lindgren [24]. Originally the negative values of the  $q_{0,1}$  constants were reported.

<sup>f</sup> Nilsson [23] ( $B_2 = 2.5751 \text{ cm}^{-1}$  and  $D_2 = 6.71 \times 10^{-4} \text{ cm}^{-1}$ ).

<sup>g</sup> Holst and Hulthén [20] ( $B_2 = 2.6028 \text{ cm}^{-1}$  and  $D_2 = 6.96 \times 10^{-4} \text{ cm}^{-1}$ ).



#### 4.3. Molecular constants of the $C^1\Sigma^+$ state of AlD

To date, the only experimental results for the  $C^1\Sigma^+, v = 0, 1$  levels were those derived from the investigation of the  $C^1\Sigma^+ - X^1\Sigma^+$  [25, 26] and  $C^1\Sigma^+ - A^1\Pi$  [24] systems.

The current  $H_0$  and  $H_1$  constant values are about two times smaller than those presented by Balfour and Lindgren [24]. The  $H_1$  constant is larger in magnitude than  $H_0$ , by a factor of five approximately. This may suggest that the  $C^1\Sigma^+$  state exhibits a relatively pronounced anharmonicity and also that the  $D_1$  and  $H_1$  constant are slightly correlated. The last situation is typical for the analysis of the bands for which a limited number of the rotational lines with high- $J$  value are observed.

Table 6: Molecular constants (in  $\text{cm}^{-1}$ ) of the  $C^1\Sigma^+$  state of AlD.<sup>a</sup>

$v$	$T_v^b$	$B_v$	$D_v \times 10^4$	$H_v \times 10^8$	Refs.
0	44,634.25405(72)	3.345685(18)	1.3861(10)	-0.289(16)	<sup>c</sup>
		3.3479(2)	1.470(7)	-0.47(7)	<sup>d</sup>
		3.350	1.8		<sup>e</sup>
1	45,638.7414(92)	3.17060(33)	1.650(33)	-1.57(96)	<sup>c</sup>
		3.1777(8)	2.00(7)	-4(2)	<sup>d</sup>
		3.174	1.8		<sup>e</sup>
		3.162	1.53		<sup>f</sup>

<sup>a</sup> Numbers in parentheses are one standard deviation in the last digit.

<sup>b</sup> Related to the  $X^1\Sigma^+, v = 0$  level.

<sup>c</sup> This work experimental results.

<sup>d</sup> Balfour and Lindgren [24].

Originally the positive values of the  $H_{0,1}$  constants were reported.

<sup>e</sup> Grabe and Hulthén [25].

<sup>f</sup> Khan [26]. The C-X,  $1 - 0$  band origin value equals 45,639.41  $\text{cm}^{-1}$ .

## 5. Computational results and discussion

The calculated MRCI+SO (MRCI with SO coupling) potential energy curves for the three electronic states in this spectroscopic study are shown in Fig. 3. Note that the observed C-state forms the inner well of the 1st excited  $^1\Sigma^+$  state. The inset presents a more detailed view of the  $A^1\Pi$  state that confirms the presence of a barrier first identified theoretically [53] by Langhoff and co-workers. In addition, there is clearly a shallower outer well, though the observed vibrational states are both localised on the deeper, inner potential well.

The aug-cc-pV5Z MRCI+SO calculation reported here underestimates the experimental [28] bond length of the  $X^1\Sigma^+$  state by 0.8 pm, a similar accuracy [55] to that demonstrated by Shi et al. in their study of the ground state alone. The values of  $r_e$  and  $T_e$  were generated using a spline of the spin-orbit *ab initio* data. The spectroscopic constants  $\omega_e$  and  $B_e$  presented in Table 7 were both extracted through a least squares fit to the  $T_v$  and  $B_v$  (respectively) values that had been generated by solving the nuclear Schrödinger equation using the LEVEL [54] program (Version 8.2). The calculated vibrational spacings and  $B_v$  constants in the  $X^1\Sigma^+$  state are all within 1% of the measured values.

The calculated  $T_e$  for the  $A^1\Pi$  state is just  $33\text{ cm}^{-1}$  lower than the experimental value ( $26652\text{ cm}^{-1}$ ) previously reported by this group [38]. To find the ro-vibrational levels in the  $A^1\Pi$  state the complex double well structure was replaced by a single potential representing the inner well alone. The accuracy of the resulting spectroscopic constants for  $v = 0$  and 1 are better than 0.6% for the vibrational spacings and 0.5% for the rotational constants validating the approximation used. However, for vibrational levels above the lowest dissociation limit we expect the accuracy of this technique to fall and so these vibrational states are not tabulated here but the calculated vibrational separation  $G(2) - G(1)$  ( $661.8\text{ cm}^{-1}$ ) and rotational constant ( $B_2 = 2.5422\text{ cm}^{-1}$ ) are still within 1.5% and 2.5%, respectively, of the measurement by Holst and Hulthén [20]. It should be noted that  $v = 2$  does appear to lie above both spin-orbit states of the Al atom (Fig. 3). Despite only four electrons being active in the SO calculations, the computed splitting in the Al( $^2P$ ) atom is much closer to the experimental values than an earlier study [56] using the same active space but a smaller basis set.

Finally, the agreement between experiment and *ab initio* results is rather poorer for the  $C^1\Sigma^+$  state but the rotational constants are still within 2%.

The error in the vibrational spacing is around  $70 \text{ cm}^{-1}$  (6%) suggesting that the shape of the inner well in the calculated  $2^1\Sigma^+$  potential is not quite correct. This inner well has a large degree of Rydberg character and the present aug-cc-pV5Z basis set probably does not have sufficiently diffuse Gaussian functions to model this extended molecular orbital well.

The calculated Franck-Condon factors for both the  $A^1\Pi - X^1\Sigma^+$  and  $C^1\Sigma^+ - X^1\Sigma^+$  transitions are reproduced in Table 8.

Figure 3: The MRCI+SO (MRCI including spin-orbit coupling) potentials of AID calculated using the aug-cc-pV5Z basis set for the  $X^1\Sigma^+$ ,  $A^1\Pi$  and  $2^1\Sigma^+$  ( $C^1\Sigma^+$ ) electronic states. Also marked are the vibrational levels ( $N = 0$ ) investigated in this study. Inset: The  $A^1\Pi$  state in closer detail. Also marked is the approximate location (see text) of the heavily predissociated  $v = 2$  level. The twin spin-orbit limits of the  $\text{Al}(3^2\text{P})$  atom are marked as dotted lines.

Table 7: Spectroscopic constants (in  $\text{cm}^{-1}$ ) of the  $X^1\Sigma^+$ ,  $A^1\Pi$  and  $C^1\Sigma^+$  states of AlD determined from *ab initio* potential energy curves.

State	$T_e^{\text{a}}$	$\omega_e^{\text{a}}$	$B_e^{\text{a}}$	$r_e^{\text{a}}$	$v$	$T_v^{\text{b}}$	$B_v^{\text{b}}$	$D_v \times 10^{4\text{b}}$
$X^1\Sigma^+$	0.0	1230.1	3.3543	1.637	0	609.3	3.3158	0.9975
					1	1802.4	3.2408	0.9816
					2	2964.4	3.1686	0.9668
					3	4096.6	3.0988	0.9528
$A^1\Pi$	23,620.0	980.3	3.2967	1.657	0	24,093.7	3.1751	1.6012
					1	24,942.0	2.9340	2.2038
$C^1\Sigma^+$	44,183.3	1159.4	3.4756	1.611	0	44,751.7	3.3957	1.2906
					1	45,820.6	3.2379	1.4631

<sup>a</sup> From a least squares fit to the data from LEVEL [54].

<sup>b</sup> From LEVEL [54]. All  $T_v$  values are relative to the minimum of the  $X^1\Sigma^+$  state.

Table 8: Computed Franck-Condon factors for the  $A^1\Pi-X^1\Sigma^+$  and  $C^1\Sigma^+-A^1\Pi$  systems of AlD.<sup>a</sup>

$X^1\Sigma^+$	$A^1\Pi$		$C^1\Sigma^+$		$A^1\Pi$
	$v = 0$	$v = 1$	$v = 0$	$v = 1$	
$v = 0$	0.9525	0.0465	0.9149	0.0825	$v = 0$
$v = 1$	0.0373	0.7279	0.0758	0.6951	$v = 1$
$v = 2$	0.0092	0.1470			
$v = 3$	0.0008	0.0591			

<sup>a</sup> All calculations were conducted using LEVEL [54] program and the values refer to the  $R(0)$  line.

## 6. Conclusions

Fourier transform emission spectroscopy was used to obtain the high-resolution spectrum of AlD in the visible region. Eight bands belonging to the  $A^1\Pi-X^1\Sigma^+$  and  $C^1\Sigma^+-A^1\Pi$  electronic transitions were identified and analyzed. Combining the current results with previous rotational [30] and ro-vibrational [28] data allowed for an improved global fit with a new molecular constants and vibrational term values for the  $X^1\Sigma^+$ ,  $A^1\Pi$  and  $C^1\Sigma^+$  states of AlD. A new set of *ab initio* potentials calculated using the aug-cc-pV5Z basis set on the two atoms and including spin-orbit coupling are in excellent agreement with the experimental results.

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